NOTE

Solvent Effect on Carboxymethylation of Cellulose

The mixture of water and isopropyl alcohol is the ideal solvent for the preparation of carboxymethyl cellulose (CMC).[1] The effect of the proportion of isopropyl alcohol to water in the solvent on the degree of substitution and viscosity of the CMC product has been reported.[2] However, no reports that studied the mechanism of such an effect have been found. This work used the X-diffraction method to determine various crystalline structures of cellulose caused by different compositions of the solvent. The relationship between the composition of the solvent and the degree of substitution, viscosity, and molecular weight of CMC is correlated quantitatively by us.

1. MECHANISM OF THE REACTION

The carboxymethylation of cellulose is a heterogeneous reaction. Its rate is dependent upon the diffusion rate of the reagents NaOH and $ClCH_2COONa$ inside the cellulose particles. Therefore, the aggregation state of the cellulose particles plays a decisive role. If the crystalline structure of the particles is destroyed sufficiently, the particles will become looser, which will elevate the reaction rate. Natural and industrial celluloses possess a high degree of crystalline aggregation, normally about 70%, which hinders the diffusion of the reagents into the particles.

If the crystalline aggregation could not be destroyed sufficiently, the NaOH and $ClCH_2COONa$ will remain in the solvent rather than diffuse into the crystalline aggregation when carrying out the carboxymethylation for cellulose. This will also result in more byproducts and decrease the availability of the monochloroacetic acid. As shown in Figure 1, usually, the first step for the preparation of CMC from cellulose is alkalization for the cellulose for loosening the agglomeration and destroying the crystalline aggregation. This effects more activated centers (cell–O^-Na^+), which facilitates the carboxymethylation. The proportion of alcohol to water in the solvent is responsible for any change in the crystalline structure of CMC.

2. EXPERIMENTAL

a. Preparation of the Alkalized Cellulose

The mixture of a certain amount of cellulose (cell–OH) and with a certain amount (M_1 in mass) of isopropyl al-

cohol was stirred for awhile. Then, a solution of M_2 (in mass) water and M_3 (in mass) NaOH was added. The system was maintained at 30°C for 1 h to alkalize the cellulose.

b. Preparation of CMC

The solution of monochloroacetic acid in an appropriate amount of isopropyl alcohol was mixed with the alkalized cellulose and prepared, followed by filtrating the aqueous solution of sodium hydroxide (M_4 in mass). The carboxymethylation was carried out at a certain temperature for 1 h.

c. X-diffraction Analysis for the Alkalized Cellulose and CMC

The samples were desiccated prior to analysis. The test conditions were as follows: radiation, $CuK\alpha$; tube voltage, 35 K V; tube current, 25 mA; wave filtration, Ni; scattering gap, 1°; receiving gap, 0.6°; diffusion gap, 1°; time constant, 2 s; test scope, 1 k × 2.

d. Determination for Degree of Substitution, Viscosity, and Molecular Weight of CMC

The degree of substitution was determined by the method described in Ref. 3. The molecular weight of CMC was determined by the same method as that of Ref. 4. Measurement of viscosity was performed with a $ZNN-D_6$ spinning viscometer. All samples were made as follows: 0.5000 of CMC was mixed with an appropriate amount of $0.1 M$ NaCl aqueous solution to make a 0.2% (in mass) solution.

3. RESULTS AND DISCUSSION

a. X-diffraction Analysis for Alkalized Cellulose and CMC

The crystalline form of natural cellulose is cell-I, which is partially destructible by the aqueous solution of sodium hydroxide to turn into an amorphous form and to result in the formation of alkalized cellulose (cell–O^-Na^+). There exists a critical concentration for the NaOH. Below

Inside the $Cell-OH+NaOH \rightleftharpoons Cell-O^-Na^+ + H_2O$

Cellulose aggregation $Cell-O^-Na^+ + ClCH_2COONa \rightarrow Cell-OCH_2COONa$

(principal reaction)

interface

between aggregation

(and the solvent)

In the solvent

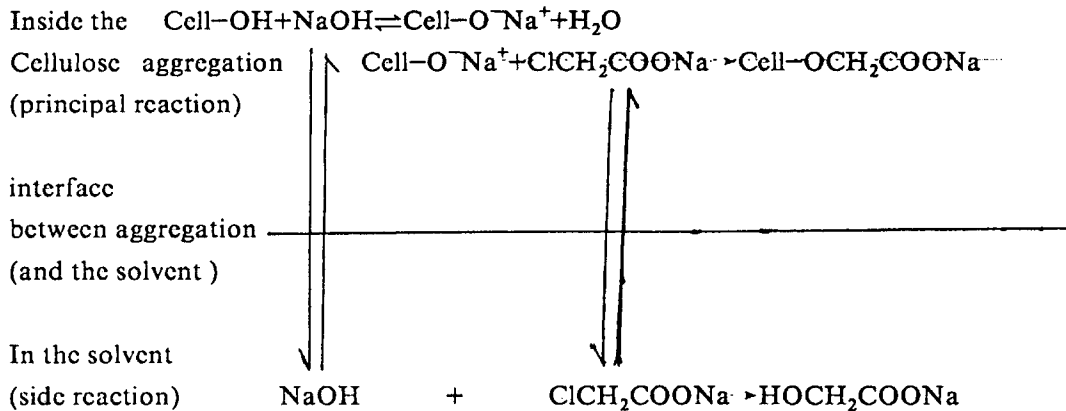(side reaction) $NaOH$ $+$ $ClCH_2COONa \rightarrow HOCH_2COONa$

Figure 1   Mechanism of the carboxymethylation of cellulose.

this value, the increase of the concentration facilitates the conversion of the cell-I form to an amorphous form. Above this value, the increase of concentration of NaOH makes the amorphous form orientate and combine into another crystalline form (cell-II). Generally, the three forms of cellulose is in equilibrium. The cell-I and cell-II forms possess their characteristic peaks in X-diffraction analysis, as shown in Figure 2.

There are external[5] and internal[6] reference methods in measuring the compositions of cell-I and cell-II forms in the cellulose. We employed the internal reference method, as shown in Figure 2. The degree of crystallization of the sample is denoted by X:

$$X = n \frac{I_k}{I_0}, \quad n = 0.75 \tag{1}$$

The percentage of the cell-II form in the crystalline aggregation is

$$C_{II} = \frac{I_{12.0}}{I_{12.0} + 0.5(I_{14.7} + I_{16.1})} \tag{2}$$

The percentage of cell-II in the sample is

$$X_{II} = X \cdot C_{II} \tag{3}$$

The percentage of cell-I is, therefore,

$$X_I = X(1 - C_{II}) \tag{4}$$

The meanings of $I_{12.0}$, $I_{16.1}$, I_0, and I_k are as shown in Figure 2.

Figure 3 shows the X-ray diffraction curves of various celluloses that were alkalized by a 4% aqueous solution of sodium hydroxide for 1 h in various solvents of isopropyl alcohol–water with a different proportion of water to al-

cohol. Natural cellulose (cell-I) gave characteristic diffraction peaks at diffraction angles of 9.0°, 14.7°, 16.1°, 22.4°, and 34.20°, whereas cell-II showed characteristic
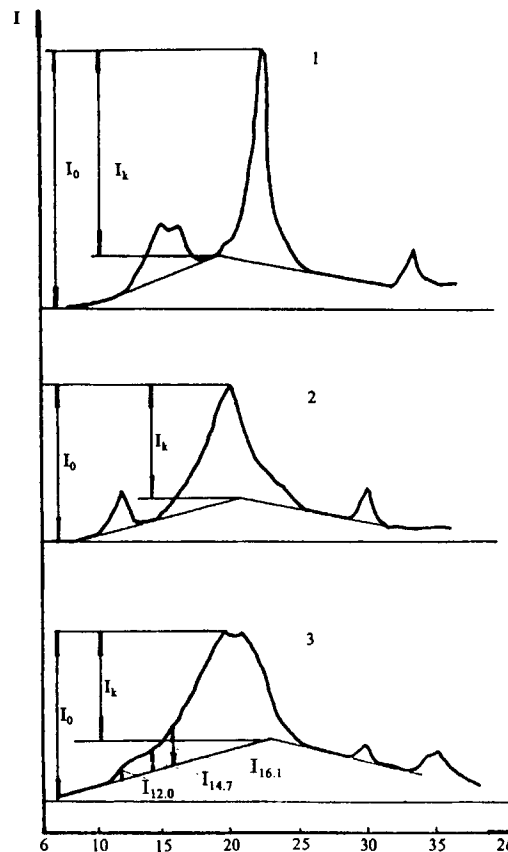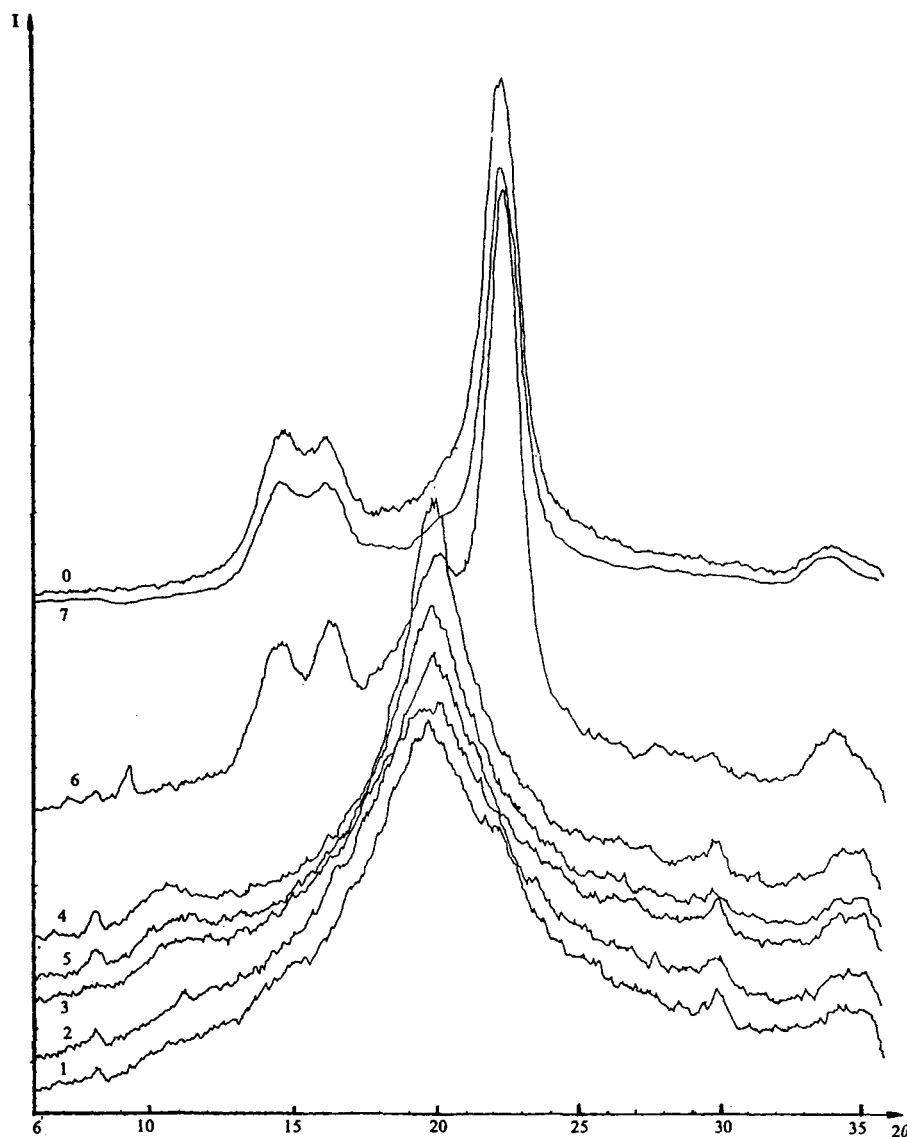
Figure 2   Distinguishing of cell-I and cell-II and the determination of crystalline structures of cell-I and cell-II samples: (1) cell-I; (2) cell-II; (3) alkalized cellulose (cell-I + cell-II).

Figure 3 The X-diffraction of alkalized celluloses under a different proportion of water to alcohol in the solvent: (0) industrial cellulose; (1–7) water content in the solvent: 5, 10, 15, 20, 25, 50, and 100%, respectively.

peaks at 9.5°, 12.0°, 20.0°, 21.5°, and 30°. In the alkalization of cell-I with sodium hydroxide, at low alcohol content or no alcohol in the solvent, there appeared no change for the characteristic peaks of cell-I. On the other hand, at higher alcohol content, the peaks at 14.7° (101) and 16.2 ($10\bar{1}$) were weakened and gradually disappeared. At $2\theta = 12°$, there appeared the characteristic peak of cell-II. The peaks of cell-I at 22.6° underwent a similar process. The cell-II peak at 20° showed up. In addition, the peak of cell-I at 34° (040) became weaker and the cell-II peak at $2\theta = 30°$ emerged. All these phenomena prove that isopropyl alcohol promotes the destruction of cell-I crystalline form and the formation of cell-II structure. The diffusion

of NaOH and water molecules into the crystal planes of cellulose is the control step for the alkalization of cellulose,[7] which can be accelerated by isopropyl alcohol.

From Figure 3, we can reach the following conclusion: The more alcohol in the solvent, the less the degree of crystallization; hence, the more aggregation destroyed. Table I presents the results of the crystalline structure of alkalized cellulose. As can be seen from this table, with the increase of alcohol content, the degree of the crystalline form (X) decreases. The molecular chains of the amorphous structure formed by the destruction of the cell-I form will partially reorientate[8] to turn into the cell-II form. However, if the alcohol content is low enough, there is

Table I   Analysis of the Crystalline Structure of Alkalized Cellulose and Industrial Cellulose

Key	Composition of Solvent Isopropyl Alcohol + Water	X	C_I	C_{II}	X_I	X_{II}
1	95 ± 5	0.375	0.718	0.282	0.269	0.105
2	90 ± 10	0.384	0.714	0.286	0.274	0.110
3	85 ± 15	0.435	0.650	0.350	0.282	0.152
4	80 ± 20	0.479	0.605	0.295	0.289	0.189
5	75 ± 25	0.541	0.728	0.262	0.393	0.147
6	50 ± 50	0.641	0.935	0.065	0.599	0.042
7	0 ± 100	0.643	1.000	0.000	0.643	0.000
0	Industrial cellulose	0.656	1.000	0.000	0.656	0.000
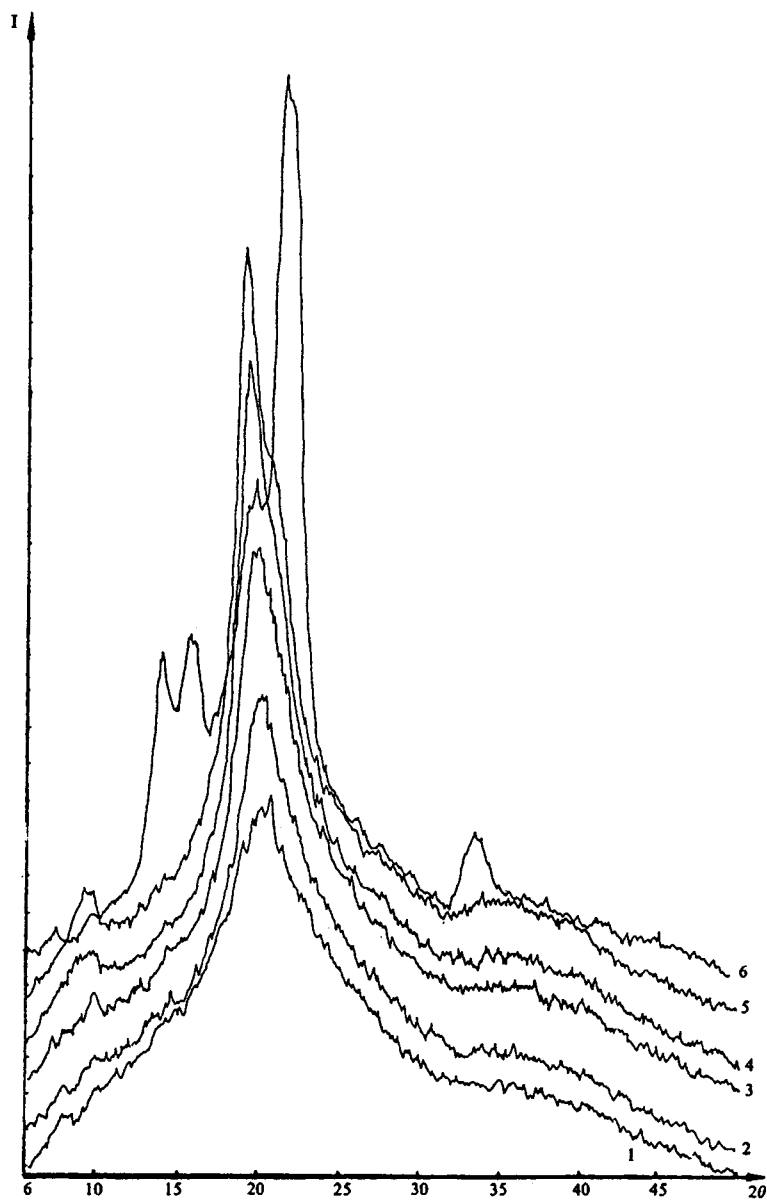
Figure 4   X-diffraction of CMC under different isopropyl alcohol contents in the solvents.

Table II   Degree of Substitution, Degree of Crystallization, Viscosity, and Molecular Weight of CMC Products from Different Solvent Compositions

	Key					
	1	2	3	4	5	6
Amount of water in the solvent (%)	5	10	15	20	25	50
Degree of crystallization	0.450	0.530	0.583	0.691	0.737	0.825
Degree of substitution (DS)	0.806	0.735	0.620	0.510	0.417	0.1
Molecular weight (DP_n)	1060	1027	1005	892	855	752
Viscosity (mPas)	16.0	10.0	5.0	4.9	4.0	3.0
Availability of monochloroacetic acid (%)	73.2	66.8	56.3	46.3	37.9	9.1

essentially no cell-II structure, whereas the cell-I structure is not destroyed on a large scale. This proves that the cell-II crystalline form is originated from the molecular chains in the amorphous form rather than cell-I. In the preparation of CMC, the cell-II form is undesirable. This is because cell-II is more compact than is cell-I, which impairs the diffusion of agents into the cellulose aggregation and, hence, decreases the reaction rate of carboxymethylation. At high alcohol content (90%), both the contents of cell-I and cell-II are fairly low. Without isopropyl alcohol, the alkalized cellulose with 4% aqueous solution of sodium hydroxide would not exhibit any change in the crystalline form compared with natural cellulose. Thus, the acceleration for destruction of cell-I can be attributed to the existence of isopropyl alcohol in the solvent. Because cell-II is from the amorphous form, any cell-II formed is evidence for the active role of isopropyl alcohol in the destruction of the cellulose crystalline structure.

The alkalized cellulose samples (nos. 1–6) underwent carboxymethylation at the same conditions that brought about the corresponding CMC products (nos. 1–6). The X-ray diffraction curves are shown in Figure 4. They also show the similar trends as in Figure 3. Table II lists the degree of crystallization for the products. It is shown that the higher the alcohol content the lower the degree of crystallization for the CMC products. However, the correlation between the degree of crystallization and the alcohol content in solvent is not as good as in the corresponding alkalized cellulose samples. This can be attributed to two facts: The crystalline structure of cellulose is destroyed further during the carboxymethylation; second, the introduction of carboxyl groups enhances the intermolecular interaction that can cause the molecules to be aligned more orderly.

b. Effect of Alcohol Content in the Solvent on Degree of Substitution, Viscosity, and Molecular Weight of the CMC Product

As the result of the low alcohol content in the solvent, the degree of substitution decreases. The availability of

monochlorinated acetic acid at 50% alcohol content, as an example (in Table III), is just 9.1%. The high water content impairs the destruction for the crystalline structure of cellulose, which hinders the diffusion of the small reagents' molecules into it and, therefore, most NaOH and $ClCH_2COOH$ remain in the solvent. In addition, the solvent of high water content is more polar than that of low water content. These factors cause more side reactions; hence, they lower the availability of monochlorinated acetic acid and the degree of substitution for CMC. On the other hand, when the alcohol content of the solvent is high, the cellulose is more sufficiently alkalized. The alkalized cellulose possesses less crystalline aggregation. This enables the reaction to be faster and to obtain a higher degree of substitution.

The molecular weight of the product has a similar relationship to alcohol content as to the other properties. At high water content, the cellulose is more decomposed by alkali. In addition, the CMC product thus obtained has a lesser degree of substitution and can be easily decomposed by alkali, which results in a low degree of polymerization for the molecular chains ($\overline{DP_n}$).

Factors that effect the viscosity of the product are the degree of substitution and degree of polymerization. A higher degree of substitution and polymerization causes higher viscosity, as expected.

4. CONCLUSION

For the solvent comprising isopropyl and water in the carboxymethylation for the cellulose, the alcohol content facilitates the destruction of cellulose crystalline structure and the diffusion of the small reagent molecules into the cellulose, which elevates the availability of the reagent for etherification. Because of the weak polarizability of isopropyl alcohol, it helps to keep the cellulose molecules to be less decomposed by alkali. This results in the increase of the degree of substitution for the CMC and effects the CMC's high resistance to alkali. Hence, the molecular weight and viscosity of the product can also be increased.

In conclusion, high alcohol content in the solvent is favorable for the carboxymethylation within the scope of our investigation.

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